



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification: C09D 5/03, C09D 167/00	A1	(11) International Publication Number: WO 00/01774
		(43) International Publication Date: 13 January 2000 (13.01.2000)

(21) International Application Number: PCT/GB99/02105

(22) International Filing Date: 02 July 1999 (02.07.1999)

(30) Priority Data:
9814534.5 03 July 1998 (03.07.1998) GB(60) Parent Application or Grant
INTERNATIONAL COATINGS LIMITED [/]; O. RING,
John [/]; O. CRAPPER, Gareth, Dale [/]; O. KITTLE, Kevin,
Jeffrey [/]; O. RING, John [/]; O. CRAPPER, Gareth, Dale [/];
O. KITTLE, Kevin, Jeffrey [/]; O. SENIOR, Janet; O.

Published

(54) Title: **POWDER COATING COMPOSITIONS**
(54) Titre: **COMPOSITIONS DE REVETEMENT EN POUDRE**

(57) Abstract

A powder coating composition of the invention comprises a film-forming polymeric component having a d(v,50) in the range of from 25 to 50 microns or a d(v,70) in the range of from 25 to 70 microns, which composition incorporates by dry-blending at least one appearance-modifying additive component and a further component comprising wax-coated silica or consisting of alumina together with aluminium hydroxide. The appearance-modifying additive may be a gloss-reducing component, a texturing component, a metallic or mica component, a colouring pigment, or a further film-forming polymeric material compatible with the first film-forming polymeric material and differing in colouration therefrom, and the further additive may be alumina together with aluminium hydroxide or wax-coated silica together with alumina and/or with aluminium hydroxide or wax-coated silica. Preferably, no more than 70 % by volume of the particles in the film-forming polymeric material are less than 50 microns. A kit of the invention comprises the individual additive components prior to mixing. The kit allows for the flexible production of a variety of finishes from a gloss powder coating composition, for example a matt or textured or metallic or sparkle finish or a matt textured finish, a matt metallic finish, an antique finish or a contrast texture or metallic sparkle finish.

(57) Abrégé

L'invention concerne une composition de revêtement en poudre comprenant un composant polymère filmogène ayant un d(v,50) de l'ordre de 25 à 50 microns et un d(v,70) de l'ordre de 25 à 70 microns. Cette composition s'obtient par mélange à sec d'au moins un adjuvant modificateur d'aspect et d'un autre composant comprenant de la silice enrobée de cire ou constitué d'alumine et d'hydroxyde d'aluminium. L'adjuvant modificateur d'aspect peut être un composant d'atténuation du brillant, un composant à effet de structure, un composant métallique ou de mica, un pigment de coloration, et un matériau polymère filmogène supplémentaire compatible avec le premier matériau polymère filmogène mais de couleur différente, cet adjuvant supplémentaire pouvant être un mélange d'alumine et d'hydroxyde d'aluminium ou un mélange de silice enrobée de cire et d'alumine, et/ou d'hydroxyde d'aluminium ou de la silice enrobée de cire. De préférence, moins de 70 % en volume des particules présentes dans le matériau polymère filmogène ont une taille inférieure à 50 microns. Un kit de l'invention comprend chacun des adjuvants avant mélange. Le kit permet la production variée d'une palette de finis obtenus à partir d'une composition de revêtement en poudre brillante, par exemple, un fini mat, à effet de structure, métallisé ou lustré, ou un fini mat à effet de structure, un fini métallisé mat, un fini antique, une texture de contraste ou un fini métallisé lustré.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C09D 5/03, 167/00	A1	(11) International Publication Number: WO 00/01774 (43) International Publication Date: 13 January 2000 (13.01.00)
(21) International Application Number: PCT/GB99/02105 (22) International Filing Date: 2 July 1999 (02.07.99) (30) Priority Data: 9814534.5 3 July 1998 (03.07.98) GB (71) Applicant (for all designated States except US): INTER- NATIONAL COATINGS LIMITED [GB/GB]; P.O. Box 20980, Oriel House, 16 Connaught Place, London W2 2ZB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): RING, John [GB/GB]; 26 Meadowvale, Darras Hall, Ponteland, Newcas- tle-upon-Tyne NE20 9NF (GB). CRAPPER, Gareth, Dale [GB/GB]; 4 Union Street, North Shields, Tyne & Wear NE30 1NL (GB). KITTLE, Kevin, Jeffrey [GB/GB]; 19 Denwick Close, Chester-le-Street, Co. Durham DH2 3TL (GB). (74) Agents: SENIOR, Janet et al.; Abel & Imray, 20 Red Lion Street, London WC1R 4PQ (GB).	(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published With international search report.	
(54) Title: POWDER COATING COMPOSITIONS		
(57) Abstract <p>A powder coating composition of the invention comprises a film-forming polymeric component having a d(v₅₀) in the range of from 25 to 50 microns or a d(v₇₀) in the range of from 25 to 70 microns, which composition incorporates by dry-blending at least one appearance-modifying additive component and a further component comprising wax-coated silica or consisting of alumina together with aluminium hydroxide. The appearance-modifying additive may be a gloss-reducing component, a texturing component, a metallic or mica component, a colouring pigment, or a further film-forming polymeric material compatible with the first film-forming polymeric material and differing in colouration therefrom, and the further additive may be alumina together with aluminium hydroxide or wax-coated silica together with alumina and/or with aluminium hydroxide or wax-coated silica. Preferably, no more than 70 % by volume of the particles in the film-forming polymeric material are less than 50 microns. A kit of the invention comprises the individual additive components prior to mixing. The kit allows for the flexibl production of a variety of finishes from a gloss powder coating composition, for example a matt or textured or metallic or sparkle finish or a matt textured finish, a matt metallic finish, an antique finish or a contrast texture or metallic sparkle finish.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GR	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

Description

5

10

15

20

25

30

35

40

45

50

55

5

10

POWDER COATING COMPOSITIONS

FIELD OF THE INVENTION

15

5

This invention relates to powder coating compositions and to their use.

20

Powder coatings form a rapidly growing sector of the coatings market. Powder coatings are solid compositions which are generally applied by an electrostatic spray process in which the powder coating particles are electrostatically charged by the spray gun and the substrate is earthed. Charging of the powder in the spray gun is effected by means of an applied voltage or by the use of friction (tribocharging). The applied composition is then heated to melt and fuse the particles and to cure the coating. The powder coating particles which do not adhere to the substrate can be recovered for re-use so that powder coatings are economical in use of ingredients. Also, powder coating compositions are generally free of added solvents and, in particular, do not use organic solvents and are accordingly non-polluting.

25

30

35

Powder coating compositions generally comprise a solid film-forming resin, usually with one or more colouring agents such as pigments, and optionally also contain one or more performance additives. They are usually thermosetting, incorporating, for example, a film-forming polymer and a corresponding curing agent (which may itself be another film-forming polymer).

40

20

45

The compositions are generally prepared by intimately mixing the ingredients (including colouring agents and performance additives) for example in an extruder, at a temperature above the softening point of the film-forming polymer(s) but below a temperature at which significant pre-reaction would occur. The extrudate is usually

50

55

5

- 2 -

10

rolled into a flat sheet and comminuted, for example by grinding to the desired particle sizes ("micronising").

15

The particle size distribution required for most commercial electrostatic spray apparatus is up to 120 microns, often between 10 and 120 microns, with a mean particle size within the range of 15 to 75 microns, preferably 25 to 50 microns, more especially 20 to 45 microns.

20

BACKGROUND TO THE INVENTION

25

10 Currently, powder coating manufacturing methods allow the manufacturer to offer commercially a range of full gloss coatings in a variety of colours. The range of products available in different finishes is, however, limited.

30

Reduction of gloss to some other lower level, for example satin gloss (55-65% gloss) or matt (< 30% gloss), is achieved by creating a surface which is rough on a microscopic scale. This surface roughness must be sufficient to cause a reduction in the specular reflection from the film by scattering the incident light; if it is visible, however, a texturing effect is achieved in the film.

35

40

In liquid paints this gloss reduction is usually achieved by the use of pigment and/or filler particles at high volume concentrations. However, this technique cannot be used as the sole route to gloss reduction in powder coatings as a high content of filler particles would lead to unacceptably too reduced a surface flow during curing.

20

45

Gloss reduction and/or texture in powder coatings may be achieved by using incompatible components or components that generate incompatibility. For example, an acrylic component and a polyester, epoxy, polyester-epoxy or polyurethane

50

25 component are incompatible, and cannot be blended to form a single (stable) phase. Incompatibility during film formation can also be achieved by using components that

55

- 3 -

are initially miscible (compatible) but that become incompatible during curing. Thus, for example, two systems of similar chemistry and approximately the same gel time are compatible, but components with different gel times are initially compatible but become incompatible as curing (and molecular weight build-up) proceeds. Materials that are incompatible during film-formation can separate into different phase domains which can give rise to incompatibility effects such as matting. Aside from this, the presence of two materials of different surface tension at the surface of the film and in discrete areas/domains can lead to surface disruption (texturing).

In practice, for gloss reduction, the procedure used is to set up reactions within the curing film such that two different gelation rates are set up within the curing matrix. With acid-functional polyesters, for example, a fast gelling (reacting) powder and a slow gelling powder may be manufactured separately using polyesters of different functionality, and mixed after the micronising stage or, more usually, the components are mixed prior to micronising. The components should have the same colour and particle size. The faster gelling domains form particles which disrupt the surface flow of the slower gelling portion of the matrix. Production of small batches of reduced-gloss coating composition, however, is uneconomic. For mixing after the micronising stage, a product called 'gloss killer' is often used, available from the company Tiger. However, this product, a clear powder coating of a conventional particle size, can be added only in limited amounts to a conventional coloured powder coating before the presence of the gloss killer can be detected from the sparkle generated by the particles of the clear gloss killer powder in the film. Therefore, the product is limited to adjusting gloss by a few percentage points. Similarly, waxes and various extenders can be used to produce satin finishes, but do not provide a matt finish. Gloss-reducing agents also include a second catalyst which will give a much faster gel time than the principal catalyst used to cure the film, e.g. for polyesters the Ciba-Geigy products "XG 125"

5

- 4 -

10

(zinc N-ethyl-N-phenyl-dithiocarbamate) and "XB 3329" (the zinc salt plus a matting wax that further reduces the gloss level, possibly through incompatibility), and, for pure epoxy and epoxy-polyester (hybrid) systems, a catalyst which has a chemical structure that causes two rates of gelation on curing, e.g. the products described in

15

5 GB 1,545,780, and including the Hüls products B55 and B68 which are adducts of pyromellitic acid and 2-phenylimidazoline.

20

For texture, a number of agents can be used to achieve different surface effects, acting by disrupting the flow of the polymer film. For a stippled finish,

micronised PTFE (polytetrafluoroethylene) is used. For a wrinkle finish, cellulose

10 acetate butyrate resin (CAB) or acylate homo- and copolymers may be used. In

25

addition, texturing agents based on high molecular weight thermoplastics are

commonly added to thermosetting powder coatings, giving rise to uniformly poor flow

across the surface, which manifests itself as a texture. PTFE is preferably added to

30

the premix before extrusion and is fully incorporated into the extrudate. However, the

15 micronised PTFE has to be prepared in a particular fashion to give batch-to-batch

consistency. CAB may be added to the finished powder or, preferably, is also added at

35

the premix stage before extrusion: it does not melt in the extruder, and the

inhomogeneous dispersion thereby produced gives rise to the texture. Some texturing

agents, however, for example Acronal 4F (T.M.), have to be added post-extrusion

40

20 since the extrusion process would render them ineffective by mixing them intimately

with the continuous phase of the coating system. However, powders containing post-

additives show inconsistency in the texturing effect on application of the powder. A

45

further post-extrusion texturing additive is the ester-modified polyether product

Powdermate 508TEX sold by the company Troy. However, this product has to be

50

25 added to a powder whose original gloss is dictated by the formulation used.

55

5

- 5 -

10

15

20

25

30

The production of metallic effect powder coatings is normally achieved by bonding the metallic pigment to the powder coating. If the pigment is incorporated into the powder coating composition with the other ingredients in the extruder the lustre effect is likely to be destroyed by the strong shear forces found in the extruders and in the subsequent micronising step. If, however, the metallic flake is simply incorporated by dry-blending, the loose metallic flakes in such processes can cause unwanted electrical discharge within the spray gun, and the presence of free metallic pigments within the powder(s) also represents a significant increase in explosion hazard. These problems are overcome in commercial operation by a mechanofusion process whereby the individual flakes of metallic pigment are bonded to the surface of conventional powder coating particles. Conventionally, however, this technique has not been applied beyond the specific field of metallic or lustre finishes.

There is accordingly a need for powder coating compositions in a variety of aesthetic finishes, including a range of reduced-gloss finishes and textured and metallic finishes, which avoid the problems mentioned above.

35

SUMMARY OF THE INVENTION

40

The present invention provides a powder coating composition which comprises a film-forming polymeric component having a $d(v,50)$ in the range of from 25 to 50 microns or having a $d(v,70)$ in the range of from 25 to 70 microns, which composition incorporates by dry blending at least one appearance-modifying additive component and a further component comprising wax-coated silica or consisting of alumina together with aluminium hydroxide.

45

50

The present invention also provides a powder coating composition which comprises a film-forming polymeric component in which no more than 75% by volume.

55

5

- 6 -

10

usually no more than 70% by volume, of the particles are less than 50 microns, which composition incorporates by dry blending at least one appearance-modifying additive component and a further component comprising wax-coated silica or consisting of alumina together with aluminium hydroxide.

15

5 The appearance-modifying additive(s) may be for example

(1) a gloss-reducing additive,

(2) a texturing agent,

20

(3) a metallic or mica pigment,

(4) a colouring pigment or pigment concentrate,

10 (5) a film-forming polymeric material compatible with the first film-forming component and differing in colouration therefrom.

25

One or more appearance-modifying additive components may, if desired, be in the form of a bonded "masterbatch" in which non-film-forming additive particles are bonded to film-forming polymeric powder material.

30

15 As will be understood in the art, the volume percentiles $d(v,x)$ indicate for a stated particle size d the percentage (x) of the total volume of the particles that lies below the stated particle size. Thus, for instance, $d(v,50)$ is the median particle size of the sample, and on a particle size distribution graph $d(v,70)$ is the point on the curve read along the particle size axis where the area under the curve below this particle size

20 represents 70% by volume of the particles. Thus, $d(v,70) = 70$ microns indicates that 70% of the particles are below 70 microns (but are not below 69 microns). (For the avoidance of doubt, it should be noted that *all* particle sizes quoted herein are by volume.) Volume percentiles are measurable by laser diffraction techniques, for example by the Malvern Mastersizer.

35

40

45

50

25 Film-forming material

(p1) having a $d(v,50)$ in the range of from 25 to 50 microns

55

5

- 7 -

10

(p2) having a d(v,70) in the range of from 25 to 70 microns and/or
(p3) in which up to 75%, usually up to 70%, of particles are below 50 microns
will generally constitute the major proportion of the total film-forming material and
preferably also the major proportion of the powder coating composition of the invention.

15

5

The use of wax-coated silica as a dry-blended additive to powder coating
compositions is described in our co-pending GB Application 9814519.6, filed 3 July
1998, and in International Application No. PCT/GB99/ (Case Reference
IP/A16/JAFFAI). The use of combinations of alumina and aluminium hydroxide as
additives for the preparation of thin film coatings has been described in WO 94/11446.

20

25

10 However, that application is concerned with thin film coatings formed using
compositions having a high proportion of particles 50 microns or less, especially 10
microns or less in size. There is no disclosure of using a film-forming component
having the above specified particle sizes. Moreover, WO 94/11446 is not concerned
with matt, texture or metallic finishes or other aesthetic effects.

30

15

The composition of the present invention, however, permits the introduction of
various additive components into a gloss powder coating composition to achieve
special effects coatings. It allows, for example, a combination of a metallic pigment
and a gloss-reducing agent or texturing agent to be incorporated simultaneously to
achieve the metallic look in any gloss level and with textured finishes. The scheme
provides a rapid and flexible means of manufacturing a range of powder coating
compositions having different appearance characteristics.

35

40

20

A different scheme for the flexible production of coloured powder coatings with
a range of different aesthetic effects is described in EP 539385 A. According to that
scheme a matting or texturing agent or other additive can be incorporated into a
powder coating composition by an agglomeration technique whereby the various
particulate components are fused or bonded to form composite particles. In contrast,

50

25

55

- 8 -

the present invention requires that at least one aesthetics additive is dry-blended into the composition.

DETAILED DESCRIPTION OF THE INVENTION

A composition of the present invention may comprise a dry-blended fluidisable mixture of for example the following particulate components:

- (i) (i) (a) a film-forming polymeric component having a $d(v,50)$ in the range of from 25 to 50 microns or having a $d(v,70)$ in the range of from 25 to 70 microns, or in which no more than 75%, usually no more than 70%, by volume of the particles are less than 50 microns, and
- (b) as minor component(s) one or more of
- (1) a gloss-reducing component,
 - (2) a texturing component,
 - (3) a metallic or mica pigment component,
 - (4) a colouring pigment or pigment concentrate, or
 - (5) a coloured film-forming polymeric component compatible with the first film-forming polymeric component, in which at least 90% by volume of the particles are no more than 20 microns,
- or
- (ii) two or more compatible film-forming polymeric components differing in colouration and each having a $d(v,50)$ in the range of from 25 to 50 microns, or having a $d(v,70)$ in the range of from 25 to 70 microns, or in which no more than 75%, usually no more than 70%, by volume of the particles are less than 50 microns, and optionally, as minor component(s), one or more of those specified in (b)(1) to (b)(5) above.

5

- 9 -

and

10

- (II) as a minor component, a further additive comprising wax-coated silica or consisting of alumina together with aluminium hydroxide.

15

Although wax-coated silica alone is contemplated as a possible further additive component, the composition may include also, for example, alumina or aluminium hydroxide, especially alumina. The combination of alumina and aluminium hydroxide should also especially be mentioned. Optionally, wax-coated silica may be used with this mixture.

20

Thus, for example, the further additive may be wax-coated silica, optionally together with alumina and/or aluminium hydroxide, or may be alumina together with aluminium hydroxide.

25

The or each film-forming polymeric material comprises at least one solid film-forming resin and includes any curing agent required therefor. Usually the film-forming polymeric component(s) mentioned above are coloured, and the colouring agent or agents (pigments and/or dyes), plus any curing agent, is extruded with the film-forming resin(s) so that particles formed therefrom comprise film-forming resin, colouring agent and, where applicable, curing agent.

30

35

Film-forming polymeric components I(i)(a) and I(ii) are generally powder coating compositions in their own right, having conventional particle size distribution, and being fluidisable. For example, such component(s) may comprise a powder having a size distribution up to 120 or 125 microns, generally in the range of from 10 to 120 microns (or 10 to 125 microns) in which preferably at least 90% by volume of particles are between 20 microns and 100 microns and usually no more than 75%, especially no more than 70%, are less than 50 microns. The mean particle size may be within the range of 15 to 75 microns, but generally no more than 60 microns, usually no more than 55 microns, and most often no more than 50 microns, but especially at

40

45

50

55

5

- 10 -

10

15

20

25

30

35

40

least 20 microns, often at least 35 microns. Most commonly the powder has a $d(v,99)$ in the range of from 60 to 120 microns. Most commonly, the mean is the range of from 25 to 50 microns, and a mean up to 45 microns should especially be mentioned. A preferred mean is in the range of from 35 to 45 microns; the corresponding $d(v,99)$ range may be 80 to 100 microns. $D(v,50)$ values of up to 45 microns, and up to 40 microns, e.g. in the ranges 25 to 30 microns and 30 to 40 microns are also of interest; corresponding $d(v,99)$ ranges may be 60 to 80 microns and 80 to 120 microns respectively. Such powders may have, for example, less than 12% and less than 8% of particles sub 10 microns respectively. $D(v,95)$ values are, for example, in the range of from 60 to 120 microns. As shown above, particle size of film-forming material may be defined in a number of different ways. $D(v,50)$ may, for example, be used for definition of particle size or, for example, the combination of $d(v,50)$ and $d(v,99)$ or $d(v,99)$ on its own may be used for definition. Alternatively, the film-forming polymeric component(s) 1(a)(i) and optionally 1(ii) to be used according to the invention may be defined by $d(v,70)$ and/or $d(v,20)$ values. For example, components 1(i)(a) and 1(ii) may comprise a powder having a $d(v,70)$ value in the range of from 25 to 70 microns with a preferred minimum $d(v,70)$ value of 30 microns, more especially 40 microns, and a preferred maximum $d(v,70)$ value of 60 microns. The $d(v,20)$ value may be, for example, 8 to 30 microns, for example 10 to 30 microns, with a preferred minimum $d(v,20)$ value of 15 microns, and a preferred maximum $d(v,20)$ value of 25 microns.

These powders usually each consist of individual particles, but composite particles formed by the fusion or bonding of two or more powders of below conventional particle size are also possible. Such products are described in EP 372860 A and EP 539385 A. If desired also, the composition may include a component in which one or more appearance-modifying additives are fused or bonded to film-forming material to form composite particles as described in EP 539385 A, or

55

- 11 -

may include two or more such components. For example, metallic or mica pigment particles may be fused or bonded to a film-forming polymeric material, preferably uncoloured. Such a "masterbatch" may then be dry blended with the remaining components of the composition. Film-forming material used in a bonded agglomerate may, for example, have the particle sizes mentioned above for components I(i)(a) and I(ii) or may, for example, be of reduced particle size. Preferably, film-forming material used for bonding to an appearance-modifying additive has a $d(v,50)$ in the range of from 15 to 50 microns (e.g. from 20 to 50 microns) or a $d(v,70)$ in the range of from 20 to 70 microns (e.g. from 20 to 50 microns); the $d(v,20)$ figure may, for example, be in the range of from 5 to 30 microns. Such material may have up to 100% by volume of particles less than 50 microns. A masterbatch may, for example, have a $d(v,50)$ in the range of from 25 to 50 microns and especially a $d(v,99)$ in the range of from 60 to 120 microns, or the particle size may be defined, for example, by a $d(v,70)$ in the range of from 25 to 70 microns or by no more than 75%, usually no more than 70%, by volume of the particles being less than 50 microns. Masterbatch powders of different particle size, for example having a finer particle size, e.g. as mentioned above for the polymeric material within the masterbatch, should also be mentioned. Alternatively, there may be two or more film-forming materials fused or bonded to form a powder, which powder is then dry blended with the remaining components of the composition.

The present invention especially provides a powder coating composition which comprises a dry-blended mixture of the following particulate components:

a) at least one coloured film-forming polymeric material

(p1) having a $d(v,50)$ in the range of from 25 to 50 microns and a $d(v,99)$ in the range of from 60 to 120 microns, or

(p2) having a $d(v,70)$ in the range of from 25 to 70 microns and a $d(v,20)$ in the range of from 8 to 30 microns, or

- 12 -

(p3) in which no more than 75%, usually no more than 70%, by volume of the particles are less than 50 microns,

and

b) at least one appearance-modifying additive component selected from

- 1) a gloss-reducing additive component,
- 2) a texturing additive component,
- 3) a metallic or mica pigment optionally bonded to uncoloured film-forming polymeric material having a $d(v,50)$ in the range of from 15 to 50 microns, or a $d(v,70)$ in the range of from 20 to 70 microns
- 4) a colouring pigment or a pigment concentrate component, or
- 5) a coloured film-forming polymeric component compatible with the first film-forming polymeric component, in which at least 90% by volume of the particles are no more than 20 microns,
- 6) a film-forming polymeric material compatible with the film-forming component (a) and of different colour therefrom, and having a particle size p_1 , p_2 or p_3 defined above,

and

- c) a further additive selected from
- alumina together with aluminium hydroxide,
- wax-coated silica together with alumina and/or aluminium hydroxide,
- wax-coated silica,

wherein the film-forming polymeric material which is component (a) and optional component (b6) and any film-forming polymeric material bonded to metallic or mica pigment in optional component (b3) and satisfying the criterion (p1), (p2) or (p3) together constitutes the major proportion of the composition by weight.

5

- 13 -

10

15

20

Preferably, in any composition of the invention the total film-forming polymeric material having a $d(v,50)$ in the range of from 25 to 50 microns, a $d(v,70)$ in the range of from 25 to 70 microns and/or in which no more than 75% by volume, usually no more than 70% by volume, of the particles are less than 50 microns, whether present as an individual component to be dry-blended in or present in a bonded masterbatch, constitute at least 60% by weight, especially at least 70% by weight, and often at least 80% by weight, of all film-forming polymeric material and preferably also of the total composition.

25

30

10

Preferably, the composition contains at least 60%, especially at least 70%, often at least 80%, by weight of coloured film-forming material of such specified particle size. By using two or more differently coloured compatible film-forming components of such a size (optionally with one or more of the components (b1) to (b5) a composition which gives a mixed colour (speckled) effect in the final coating is obtained.

35

40

15

Combinations of appearance-modifying components may be of especial interest. For example, the composition may include any two of components (b1), (b2) and (b3), (b3) often being in the form of a masterbatch. Using such combinations there can be obtained a matt texture finish (components (b1) + (b2)), a matt metallic finish (components (b1) + (b3)) or an antique finish (components (b2) + (b3)) in the final coating. A further useful combination is component (b2) together with pigment component (b4), which gives a contrast texture in the final coating.

45

The present invention also provides a kit comprising the following separate components for dry blend mixing into powder coating compositions for the preparation of powder coatings in a number of different finishes:

50

25

- at least one appearance-modifying additive component selected from
 - (1) a gloss-reducing component,
 - (2) a texturing component,

55

- 14 -

(3) a metallic or mica pigment component, and

(4) a colouring pigment or pigment concentrate component, and

(5) a coloured film-forming polymeric component having a $d(v,90)$ of no more than 20 microns,

5 and

- a further additive selected from

alumina together with aluminium hydroxide,

wax-coated silica together with alumina and/or aluminium hydroxide,

wax-coated silica,

10 that is:

(i) alumina together with aluminium hydroxide

(ii) alumina together with wax-coated silica

(iii) aluminium hydroxide together with wax-coated silica,

(iv) alumina together with aluminium hydroxide and wax-coated silica, or

15 (v) wax-coated silica,

or two or more such additives.

35 Preferably the kit includes all of components (1), (2) and (3) and optionally also component(s) selected from (4) and (5).

40 Generally, the particle size of the components is such that when added to a powder coating composition the composition remains fluidisable, although one or more components may alternatively be comminuted before use, for example together with the powder coating chip material when it is milled to powder form.

45 By using a kit of the present invention, the manufacturer can produce a variety of finishes quickly and easily from a finished gloss powder coating composition or from its precursor chip material or from a combination of two or more such compositions/ materials by using a selection from a limited number of other components.

5

- 15 -

10

15

Where appropriate, an appearance-modifying additive component in the kit is optionally in the form of a bonded masterbatch (that is, a non-film-forming additive is bonded to film-forming polymeric material) and/or the kit includes an uncoloured polymeric film-forming component having a $d(v,50)$ in the range of from 15 to 50 microns and/or a $d(v,70)$ in the range of from 20 to 70 microns for bonding with a non-film-forming appearance-modifying additive if desired. Thus, for example, the kit may include

20

- metallic or mica pigment and
- an uncoloured film-forming polymeric component for optional bonding therewith or a pre-bonded metallic or mica masterbatch.

10

25

This would give, for example, the option of incorporating mica or bonded mica or mica and uncoloured polymeric component into the finished powder coating composition; different effects would be achieved in the resulting coating.

30

The present invention has the advantage of reducing stocking levels and manufacturing capacity. It enables a very rapid and flexible service to be provided to the customer, allowing for the possibility of providing small quantities of powder coating compositions economically on request.

35

DESCRIPTION OF PREFERRED EMBODIMENTS

40

20

In one embodiment of the invention a film-former having a different gel time from that of the main film-former and initially compatible therewith is used to reduce gloss: for example for acid-functional polyester (component (a)), an acid-functional polyester with a different functionality and hence different gel time may be used. For polyurethane systems using hydroxy-functional polyesters cured with an isocyanate (typically isophorone diisocyanate component (a)), a hydroxy-functional polyester with

50

55

5

- 16 -

10

a radically different functionality (e.g. a hydroxy-functional polyester with a functionality of 7 added to one with a functionality of 2) and hence a different gel time, can be used.

15

Another possibility is to employ as gloss-reducing additive b1) a polymeric material that is *per se* incompatible with the polymeric film-forming material a), for example, for a polyester an acrylic polymer as appearance-modifying additive.

20

The gloss-reducing additive is preferably uncoloured or, for example, the same colour as the first component. Alternatively, it may be formulated in a colour

10

appropriate for dry blending with a number of different colours. For example, a red gloss-reducing additive could be prepared for dry blending with a range of red gloss

25

coating compositions, a white gloss-reducing additive could be prepared for dry blending with a range of blue gloss coating compositions, etc..

30

In a preferred embodiment film-forming component (a) is a polyester and the gloss-reducing agent is an uncoloured powder coating composition comprising a polyester of higher functionality, which composition has been milled to a fine powder.

15

Increased amounts of this film-forming component leads to increased reduction of gloss and, in comparison with conventional gloss-reduction methods, by reducing the size of the uncoloured powder higher percentages of the gloss-reducing agent can be added to the coloured powder coating to reduce its gloss.

35

40

Suitably, the gloss-reducing agent is present in an amount up to 30%, preferably up to 20%, by weight, relative to the weight of the whole composition.

45

A gloss-reducing agent having at least 90% by volume of particles < 20 microns, more especially at least 90% by volume < 10 microns, and with a preferred mean particle size in the range of from 1.5 to 12 microns, for example 3 to 5 microns or 8 to 12 microns should be mentioned. Gloss-reducing agents having < 90% by volume < 20 microns may also be used. Advantageously the gloss-reducing agent (b1) has a particle size 90% by volume < 50 microns, e.g. 90% by volume < 40 microns, and with a

50

55

5

- 17 -

10

15

20

25

mean particle size preferably <30 microns, advantageously in the range of from 5 to 25 microns, for example in the range of from 8 to 23 microns, e.g. substantially 18 microns. It is possible, for example, to add up to 15%, e.g. between 5 and 15%, of this reduced-size polyester additive to reduce the gloss of the coloured powder coating to 70 gloss units (a satin finish) or 20 gloss units (a matt finish) from the traditional full gloss of 90 gloss units. Using a fine powder coating to modify a conventional powder coating might be expected to alter its application properties. The fine particles together with larger-sized particles would be expected to cause problems such as spitting and surging through application equipment, and the internal bi-polar charging would mean that gloss variations would occur across the coated article. The coating composition of the present invention, however, gives uniformity of product even after transportation and spraying.

30

If desired, a film-forming gloss-reducing additive may be bonded to a different appearance-modifying additive to form composite particles as mentioned above.

15

35

In a further embodiment conventional texturing agents may be dry blended in; those agents include the non-film-forming polymer PTFE, and CAB or other suitable film-forming polymer. The ester-modified polyester oligomer texturing agent manufactured by Troy may also be used. Such additives are known dry blend texturing additives.

40

20

Suitably, the texturing agent is present in an amount up to 5% by weight, relative to the weight of the whole composition.

45

In a further embodiment, aluminium and a number of other metals and alloys, e.g. stainless steel, copper, tin, bronze and brass, may be used to produce what are referred to as 'lustre' or 'glamour' finishes, or 'flop', polychromatic, and sparkle effects.

50

25

('Flop' is the ability to change colour when viewed at different angles. This capability is directly related to flake orientation in the film.) Mica pigments may also be used; these

55

5

- 18 -

10

are thin platelets of the natural mineral mica coated with titanium dioxide and/or iron(III)oxide.

15

Suitably, the metallic or mica pigment is used, for example, in an amount up to 10% by weight, relative to the weight of the whole composition.

20

5 If desired, mica or a metallic pigment may be fused or bonded to powder as described for example in EP 539 385 A, preferably by mechanofusion, and then incorporated by dry blending with powder components a) and c) (and optionally other components listed under (b) above), to achieve special effects (for example, a lustre or metallic sparkle not achievable by conventional means). It is often convenient for the 10 film-forming material incorporated in the masterbatch to be uncoloured. Suitably, the bonded "masterbatch" contains 2 to 40 %, for example about 25 %, by weight of mica or metallic pigment, and is used in an amount such that the metallic or mica pigment is present in an amount of up to 10% by weight, relative to the weight of the composition. 25 This process is to be contrasted with the prior practice of bonding, for example, 3% of 30 the metallic pigment to the whole batch of standard powder. 15

35

The composition may also include a colouring pigment (b4) in an amount of up to 5% by weight, relative to the weight of the whole composition. Incorporation of pigment for example together with a texturing additive gives a contrast texture finish.

40

Pigment may, for example, be in the form of a pigment masterbatch. Pigment 20 masterbatches, comprising the pigment pre-dispersed in very high concentrations in polymer material which is *per se* non-film-forming, are generally available commercially in chip or powder form. When applied to a substrate and heated, such 45 polymers can melt and wet out on the substrate, but the masterbatches are not formulated as film-formers and contain no curing agent.

50

25 A film-forming component compatible with the first, film-forming, component (a) and differing in colouration therefrom may also be dry blended into the composition.

55

5

- 19 -

10

Usually the first film-forming component (a) is coloured and any film-forming polymer component(s) are differently coloured, although such a further film-forming component may alternatively be uncoloured.

15

Such a component may, for example, be a conventional powder coating composition. With one or more film-forming components (b6) having a particle size as defined for the film-forming component (a) and different in colour from component (a), a speckled finish is achieved, the result varying according to the relative amounts of the film-forming components. Components (a) and, if present, (b6) preferably constitute at least 60%, especially at least 70%, often at least 80%, by weight of the composition.

20

Pigment component (b4) or additional film-forming component (b5) compatible with the first film-forming component (a) may alternatively be used for colour tinting, for example of an uncoloured powder coating composition (a) or, especially if the additional component is close in colour to the film-forming component (a), for colour adjustment of that composition. In each case, if the amount and particle size of this additional component are sufficiently small the differences in colour arising from differently coloured particles in the final coating cannot be discerned by the unaided human eye and a visually homogeneous coating will result. For such purposes the component is generally added in an amount of up to 5%, preferably up to 1%, by weight, based on the weight of the total composition; suitably the component has a particle size such that least 90% by volume of particles are below 20 microns, preferably below 10 microns, and the mean particle size is within the range of from 1.5 to 12 microns. The possibility of adjusting colour by this means also assists product flexibility.

25

30

35

40

45

Thus, non-film-forming appearance-modifying additives (present as separate particulate components or in a bonded masterbatch powder component) may be, for example, a texturing agent (if present, generally 0.5% by weight or more of the composition), a metallic or mica pigment (if present, generally 0.1% by weight or more

50

55

5

- 20 -

10

of the composition) and/or pigment or pigment concentrate (if present, generally 0.01% by weight or more of the composition).

15

Film-forming appearance-modifying additives (present as separate particulate components or in a bonded masterbatch powder component) may be, for example, a gloss-reducing film-forming additive (if present, generally 0.5% by weight or more of the composition) and/or a coloured film-forming polymeric component compatible with film-forming component (a) (if present, generally 0.01% by weight or more of the composition).

20

As further particulate component (c) the following combinations should be mentioned:

25

- i) alumina together with aluminium hydroxide
- ii) alumina together with wax-coated silica
- iii) alumina together with aluminium hydroxide and wax-coated silica
- iv) aluminium hydroxide together with wax-coated silica
- v) wax-coated silica.

30

The combinations (i), (ii) and (iii) should especially be mentioned. The combinations

35

alumina pre-mixed with aluminium hydroxide,

alumina with aluminium hydroxide and wax-coated silica

40

in particular have given good results.

45

The term "coating" as used herein in relation to silicas for use according to the invention includes impregnation of porous silica materials, and the expression "coated silica" is to be understood accordingly.

50

The term "silica" as used herein includes materials obtained by pyrogenic and, preferably, wet processes leading to precipitated silicas or silica gels, as well as, in principle, mixed metal-silicon oxides and naturally-occurring materials such as, for

55

5

- 21 -

10

example, diatomaceous earth. Silicas for use according to the invention will in general have an amorphous structure. The term "silica" includes silicic acid materials. Silicates also come into consideration.

15

5

A preferred material comprises micronised silica gel.

The term "wax" as used herein includes:

20

- i) Natural animal waxes (for example, beeswax, lanolin);
- ii) Natural vegetable waxes (for example, carnauba wax);
- iii) Natural petroleum waxes (for example, paraffin wax, microcrystalline wax);
- iv) Synthetic waxes (for example, ethylenic polymers and polyol ether-esters).

10

Mineral waxes other than petroleum waxes may also come into consideration.

25

An important group of waxes for use in accordance with the invention comprises esters of long-chain aliphatic alcohols (typically C_{18} and above) with long-chain fatty acids (typically C_{16} and above). Such esters and acids are preferably straight-chain compounds, and may be saturated or unsaturated. Examples of acids which may be used include stearic acid, palmitic acid and oleic acid and mixtures of two or more thereof.

35

Waxes derived from long-chain aliphatic compounds as described above may include hydrocarbons.

40

20

In addition to esters of the long-chain acids as described above there may be mentioned salts such as, for example, aluminium stearate.

45

25

Preferred wax materials for use in accordance with the invention are materials which have good compatibility with the polymer component(s) of the powder coating composition, that is to say, materials which can be mixed homogeneously with the polymers without significant phase separation. It will be found that some wax materials (for example, halogenated waxes) are in general not compatible in this sense with the powder coating polymer(s). The use of such materials would be expected to give rise

50

55

5

- 22 -

10

to defects in the surface appearance of the finished applied coating, and is accordingly not recommended.

15

Wax-coated silicas suitable for use in accordance with the invention include commercially available materials such as, for example, GASIL 937 ex Crosfield (a silica gel coated with microcrystalline paraffin wax) and OK 607 ex Degussa (a similar material with a coating which also includes a short-chain [C₆] saturated amine or alkyl ammonium component).

20

Coating of the silica material may be effected by methods known in the art, for example, by co-milling of the silica with a solid wax material, or by admixing the silica material with a wax material dissolved in a suitable solvent which is then evaporated.

25

The amount of wax coated onto the silica may, for example, be in the range of from 2 to 10% by weight, based on the weight of the silica.

30

Further information concerning wax-coated silicas for use in accordance with the invention may be found in U.S. Patent Specifications Nos. 3 607 337 and 3 816 154, and in WO 97/08250..

35

In addition to wax-coated silica, a powder coating composition of the invention may incorporate, also by dry blending, aluminium oxide and/or aluminium hydroxide, preferably aluminium oxide or aluminium oxide and aluminium hydroxide. Aluminium oxy-hydroxide may be used in addition to or instead of aluminium hydroxide.

40

Alternatively, a combination of aluminium oxide and aluminium hydroxide alone may be used.

45

It is believed that any of the main structural types of these materials may be used, that is to say:

50

25

α - Al₂O₃ Corundum

α - Al(OH)₃ Bayerite

55

5

- 23 -

 γ - Al_2O_3

10

 γ - $\text{Al}(\text{OH})_3$ Gibbsite

Preference may be given to γ structural types.

15

5 The total content of the further component (c) incorporated in a powder coating composition of the invention may in general be up to 5% by weight, and generally at least 0.002%, usually at least 0.05%, by weight, e.g. in the range of from 0.1 to 5% by weight, based on the total weight of the composition, and advantageously up to 2% by weight, especially up to 1.5% by weight, and preferably at least 0.2% by weight, and more especially 0.3 to 1% by weight. Especial mention should be made of

10 compositions in which there is a total content of no more than 10% by weight of non-film-forming material present as separate component(s) and (in the case of appearance-modifying additives) optionally bonded in masterbatch component(s).

25

30

The proportion of wax-coated silica incorporated in a powder coating composition of the invention may in general be in the range of from 0.002 to 2.0% by weight, based on the total weight of the composition, advantageously from 0.02 to 1.5% by weight and preferably from 0.04 to 1.0% by weight, more especially at least 0.2% by weight, especially 0.3 to 0.7% by weight, for example, 0.3 to 0.5% by weight.

35

40

In the case in which one of the dry-blended additives is alumina, the proportion of alumina incorporated may be at least 0.01% by weight, advantageously at least 0.02% by weight and generally in the range of from 0.2 to 0.4% by weight based on the total composition. Because of its relatively intense effect on electrostatic phenomena, the proportion of alumina will not normally exceed 1.0% by weight.

45

Typically, in the case in which the component is alumina together with aluminium hydroxide, the content of the aluminium hydroxide will not exceed 5% based

50

55

5

- 24 -

10

on the total composition, and will in general not exceed 3% based on the total composition, and in the preferred case will not exceed 1%. Ratios of alumina to aluminium hydroxide, from 90:10 to 10:90, e.g. 12:88 to 45:55, should especially be mentioned.

15

5 In the case in which the powder coating composition includes dry-blended additives comprising wax-coated silica and aluminium oxide, the relative proportions of silica to aluminium oxide may in general be in the range of from 99:1 to 1:99, advantageously from 80:20 to 20:80, and preferably 70:30 to 30:70, for example 50:50.

20

10 In the case in which the dry-blended additives comprise wax-coated silica and aluminium hydroxide, the relative proportions of silica to the aluminium hydroxide may in general be from 99:1 to 30:70, advantageously from 90:10 to 40:60, preferably from 80:20 to 50:50, for example 65:35.

25

30 In the case in which the dry-blended additives comprise wax-coated silica, aluminium oxide and aluminium hydroxide, the relative proportions of the additives may in general be as follows:

30

35

	SiO ₂	Al ₂ O ₃	Al(OH) ₃
	<hr/>	<hr/>	<hr/>
	1 to 98%	1 to 98%	1 to 70%
advantageously	5 to 50%	10 to 90%	1 to 60%
40 20 preferably	10 to 30%	20 to 85%	1 to 55%

Each dry-blended additive (c) is generally in finely divided form and may have a particle size up to 5 microns, or even up to 10 microns in some cases. Preferably, however, the particle size is not greater than 2 microns, and is more especially not greater than 1 micron.

45

50 25 When component (c) comprises two or more products it is strongly preferred for at least this component to be pre-mixed, preferably intimately and homogeneously by a

50

55

5

- 25 -

10

high shear technique, before being dry-blended with the composition. The case where component (c) includes wax-coated silica, and that material is incorporated and dry-blended separately, should also be mentioned.

15

As already mentioned, a powder coating composition according to the invention may contain a single film-forming powder component comprising one or more film-forming resins or may comprise a mixture of two or more such components, a component optionally being in the form of a masterbatch in which film-forming material is bonded to non-film forming material.

20

25

The film-forming resin (polymer) acts as a binder, having the capability of wetting pigments and providing cohesive strength between pigment particles and of wetting or binding to the substrate, and melts and flows in the curing/stoving process after application to the substrate to form a homogeneous film.

30

The or each film-forming powder coating component of a composition of the invention will in general be a thermosetting system, although thermoplastic systems (based, for example, on polyamides) can in principle be used instead.

35

When a thermosetting resin is used, the solid polymeric binder system generally includes a solid curing agent for the thermosetting resin; alternatively two co-reactive film-forming thermosetting resins may be used.

40

The film-forming polymer used in the manufacture of a film-forming component of a thermosetting powder coating composition according to the invention may be one or more selected from carboxy-functional polyester resins, hydroxy-functional polyester resins, epoxy resins, and functional acrylic resins.

45

50

A film-forming component of the composition can, for example, be based on a solid polymeric binder system comprising a carboxy-functional polyester film-forming resin used with a polyepoxide curing agent. Such carboxy-functional polyester systems are currently the most widely used powder coatings materials. The polyester

55

5

- 26 -

10

15

generally has an acid value in the range 10-100, a number average molecular weight Mn of 1,500 to 10,000 and a glass transition temperature Tg of from 30°C to 85°C, preferably at least 40°C. The poly-epoxide can, for example, be a low molecular weight epoxy compound such as triglycidyl isocyanurate (TGIC), a compound such as diglycidyl terephthalate condensed glycidyl ether of bisphenol A or a light-stable epoxy resin. Such a carboxy-functional polyester film-forming resin can alternatively be used with a bis(beta-hydroxyalkylamide) curing agent such as tetrakis(2-hydroxyethyl) adipamide.

20

25

30

35

40

45

50

55

Alternatively, a hydroxy-functional polyester can be used with a blocked isocyanate-functional curing agent or an amine-formaldehyde condensate such as, for example, a melamine resin, a urea-formaldehyde resin, or a glycol ural formaldehyde resin, for example the material "Powderlink 1174" supplied by the Cyanamid Company, or hexahydroxymethyl melamine. A blocked isocyanate curing agent for a hydroxy-functional polyester may, for example, be internally blocked, such as the uret dione type, or may be of the caprolactam-blocked type, for example isophorone diisocyanate.

As a further possibility, an epoxy resin can be used with an amine-functional curing agent such as, for example, dicyandiamide. Instead of an amine-functional curing agent for an epoxy resin, a phenolic material may be used, preferably a material formed by reaction of epichlorohydrin with an excess of bisphenol A (that is to say, a polyphenol made by adducting bisphenol A and an epoxy resin). A functional acrylic resin, for example a carboxy-, hydroxy- or epoxy-functional resin can be used with an appropriate curing agent.

Mixtures of film-forming polymers can be used, for example a carboxy-functional polyester can be used with a carboxy-functional acrylic resin and a curing agent such as a bis(beta-hydroxyalkylamide) which serves to cure both polymers. As further possibilities, for mixed binder systems, a carboxy-, hydroxy- or epoxy-functional

5

- 27 -

10

acrylic resin may be used with an epoxy resin or a polyester resin (carboxy- or hydroxy-functional). Such resin combinations may be selected so as to be co-curing, for example a carboxy-functional acrylic resin co-cured with an epoxy resin, or a carboxy-functional polyester co-cured with a glycidyl-functional acrylic resin. More usually,

15

5 however, such mixed binder systems are formulated so as to be cured with a single curing agent (for example, use of a blocked isocyanate to cure a hydroxy-functional acrylic resin and a hydroxy-functional polyester). Another preferred formulation involves the use of a different curing agent for each binder of a mixture of two polymeric binders (for example, an amine-cured epoxy resin used in conjunction with a 10 blocked isocyanate-cured hydroxy-functional acrylic resin).

25

Other film-forming polymers which may be mentioned include functional fluoropolymers, functional fluorochloropolymers and functional fluoroacrylic polymers, each of which may be hydroxy-functional or carboxy-functional, and may be used as 30 the sole film-forming polymer or in conjunction with one or more functional acrylic, 15 polyester and/or epoxy resins, with appropriate curing agents for the functional polymers.

35

Other curing agents which may be mentioned include epoxy phenol novolacs and epoxy cresol novolacs; isocyanate curing agents blocked with oximes, such as 40 isophorone diisocyanate blocked with methyl ethyl ketoxime, tetramethylene xylene 20 diisocyanate blocked with acetone oxime, and Desmodur W (dicyclohexylmethane diisocyanate curing agent) blocked with methyl ethyl ketoxime; light-stable epoxy 45 resins such as "Santolink LSE 120" supplied by Monsanto; and alicyclic poly-epoxides such as "EHPE-3150" supplied by Daicel.

45

Examples of pigments which may be used are inorganic pigments, such as, for 50 25 example, titanium dioxide white, red and yellow iron oxides, chrome pigments and carbon black, and organic pigments such as, for example, phthalocyanine, azo,

50

55

5

- 28 -

10

anthraquinone, thioindigo, isodibenzanthrone, triphendioxane and quinacridone pigments, vat dye pigments and lakes of acid, basic and mordant dyestuffs. Dyes may be used instead of or as well as pigments. Each coloured film-forming component of the coating composition may contain a single colorant (pigment or dye) or may contain

15

5 more than one colorant.

20

The composition of the invention may also include one or more extenders or fillers, which may be used *inter alia* to assist opacity, whilst minimising costs, or more generally as a diluent. The following ranges should be mentioned for the total pigment/filler/extender content of the film-forming polymeric material (e.g. (a) or (b6)):

10 0% to 55% by weight, 0% to 50% by weight, 10% to 50% by weight, 0% to 45% by weight, and 25% to 45% by weight. Of the total pigment/filler/extender content, a pigment content of $\leq 40\%$ by weight of the film-forming polymeric material may be used. Usually a pigment content of 25-30% is used, although in the case of dark colours opacity can be obtained with $< 10\%$ by weight of pigment.

25

30

15 The powder coating composition may also contain one or more performance additives such as, for example, a flow-promoting agent, a plasticiser, a stabiliser, for example a stabiliser against UV degradation, or an anti-gassing agent, such as benzoin. Such additives are known and standard additives for use in powder coating compositions. The following ranges should be mentioned for the total performance

20 additive content of a film-forming polymeric material: 0% to 5% by weight, 0% to 3% by weight, and 1% to 2% by weight.

35

40

45 In general, these colouring agents and performance additives will be incorporated into the film-forming material before and/or during the extrusion or other homogenisation process, and not by dry blending. The film-forming component(s) may

25 be manufactured by a conventional melt extrusion and micronising process, optionally

50 followed by a fusion or bonding process as described in EP 539385A. Thus, for

45

50

55

5

- 29 -

10

example, two or more separate powders may be formed by extrusion and micronising and then fused or bonded into composite particles. In a different embodiment, melt extrusion and micronising may be followed by fusion or bonding to a non-film-forming additive to form an appearance-modifying component (b).

15

5 The additive components of the invention (components (b) and (c)) may be incorporated in the powder coating composition by any available dry-blending method, for example:

20

(a) injection at the mill, with the chip and additive(s) fed into the mill simultaneously;

10

(b) introduction at the stage of sieving after milling; and

25

(c) post-production blending in a "tumbler" or other suitable mixing device.

In one embodiment, components (a) and (b) are mixed together and a pre-mixed component (c) is then added before discharge from the mixer.

30

15 Thus in one embodiment of the present invention, a range of basic coloured powder coating compositions is produced, conventionally, in a conventional melt extrusion step, and a wide range of different finishes can then be produced easily on demand by a simple mixing step, so that the production of small quantities becomes commercially feasible.

35

40

20 The gloss-reducing component may, for example, be a pre-prepared uncoloured coating composition of fine particle size or one of conventional size which is reduced in size just prior to use. Advantageously, for any particular type of film-forming chemistry (e.g. acid-functional polyester, hydroxy-functional polyester), the kit of the invention includes a "universal" gloss-reducing component suitable for all conventional powder coating compositions of that chemistry. Other appearance-

45

50

25 modifying additives may be for example commercially available additives or prepared

55

- 30 -

therefrom by a bonding process as in the case of the metallic or mica masterbatch discussed above.

A powder coating composition according to the invention may in principle be applied to a substrate by any suitable process of powder coating technology, for example by electrostatic spray coating, or by fluidised-bed or electrostatic fluidised-bed processes.

After application of the powder coating composition to a substrate, conversion of the resulting adherent particles into a continuous coating (including, where appropriate, curing of the applied composition) may be effected by heat treatment and/or by radiant energy, notably infra-red, ultra-violet or electron beam radiation.

The powder is usually cured on the substrate by the application of heat (the process of stoving), usually for a period of from 5 to 30 minutes and usually at a temperature in the range of from 150 to 220°C, although temperatures down to 90°C may be used for some resins, especially epoxy resins; the powder particles melt and flow and a film is formed. The curing times and temperatures are interdependent in accordance with the composition formulation that is used, and the following typical ranges may be mentioned:

<u>Temperature/°C</u>	<u>Time</u>
280 to 100*	10 s to 40 min
250 to 150	15 s to 30 min
220 to 160	5 min to 20 min

* Temperature down to 90°C may be used for some resins, especially certain epoxy resins.

The invention also provides a process for forming a coating on a substrate, which comprises applying a composition according to the invention to a substrate, for

5

- 31 -

example by an electrostatic spray coating process, and heating the applied composition to melt and fuse the particles and cure the coating.

10

The film may be any suitable thickness. For decorative finishes, film thicknesses as low as 20 microns should be mentioned, but it is more usual for the film thickness to fall within the range 25-120 microns, with common ranges being 30-80 microns for some applications, and 60-120 microns or, more preferably, 60-100 microns for other applications, while film thicknesses of 80-150 microns are less common, but not rare.

15

20

The substrate may comprise a metal, a heat-stable plastics material, wood, glass, or a ceramic or textile material. Advantageously, a metal substrate is chemically or mechanically cleaned prior to application of the composition, and is preferably subjected to chemical pre-treatment, for example with iron phosphate, zinc phosphate or chromate. Substrates other than metallic are in general preheated prior to application or, in the case of electrostatic spray application, are pretreated with a material that will aid such application.

25

30

15

The following Examples illustrate the invention:-

35

EXAMPLES

40

20

The aluminium oxide used in the Examples was Aluminium Oxide C, ex Degussa, mean particle size < 0.2 microns; the aluminium hydroxide used was Martinal OL 103C, ex Omya Croxton & Garry, mean particle size 0.8 microns; and the wax-coated silica used was Gasil 937, ex Crosfield, mean particle size 6.5 microns (a micronised silica gel coated with microcrystalline paraffin wax).

45

25

The particle size distribution data reported in the Examples was obtained using the Mastersizer X laser light-scattering device from Malvern Instruments.

50

55

5

- 32 -

Individual components used in the Examples were prepared as follows:-

10

Blue Polyester Gloss Base Composition

15

	Phthalocyanine Blue Pigment	18 g
5	Black Iron Oxide Pigment	8 g
	Titanium Dioxide	17 g
	Filler (Barium Sulphate)	100 g
20	Filler (Calcium Carbonate)	200 g
	Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g ⁻¹)	618 g
10	Hydroxyalkylamide Curing Agent (i.e. PRIMID, ex EMS Grilon)	23 g
25	Acrylic Flow Modifier	8 g
	Benzoin	4 g
	Polyethylene Wax	4 g

30

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of d(v,20) = 20 microns, d(v,50) = 38 microns, d(v,70) = 52 microns, d(v,95) = 79 microns, d(v,99) = 94 microns; 68% of particles were less than 50 microns.

35

White Polyester Gloss Base Composition

40

20	Titanium Dioxide	300 g
	Filler (Barium Sulphate)	100 g
	Filler (Calcium Carbonate)	70 g
45	Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g ⁻¹)	756 g
	Hydroxyalkylamide Curing Agent	28 g
25	Acrylic Flow Modifier	8 g
50	Benzoin	4 g

55

Polyethylene Wax

4 g

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of $d(v,20) = 22$ microns, $d(v,50) = 40$ microns, $d(v,70) = 52$ microns, $d(v,95) = 78$ microns, $d(v,99) = 99$ microns; and 64% < 50 microns.

Yellow Polyester Gloss Base Composition

		164 g
	Titanium Dioxide	7 g
	Yellow Iron Oxide Pigment	29 g
10	Yellow Quinophthalone Pigment	140 g
25	Filler (Calcium Carbonate)	621 g
	Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g ⁻¹)	23 g
	Hydroxyalkylamide Curing Agent	8 g
30	Acrylic Flow Modifier	4 g
15	Benzoin	4 g
	Polyethylene Wax	

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of $d(v,20) = 20$ microns, $d(v,50) = 40$ microns, $d(v,70) = 51$ microns, $d(v,95) = 82$ microns, $d(v,99) = 102$ microns; and 63% < 50 microns.

Grey Polyester Gloss Base Composition

		9 g
45	Carbon Black Pigment	76 g
	Titanium Dioxide	15 g
25	Yellow Iron Oxide Pigment	210 g
50	Filler (Barium Sulphate)	

- 34 -

5	Filler (Calcium Carbonate)	100 g
10	Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g ⁻¹)	561 g
	Hydroxyalkylamide Curing Agent	21 g
	Benzoin	4 g
15	5 Polyethylene Wax	4 g

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of d(v,20) = 19 microns, d(v,50) = 40 microns, d(v,70) = 51 microns, d(v,95) = 80 microns, d(v,99) = 97 microns; and 67% < 50 microns.

Brown Polyester Gloss Base Composition

25	Carbon Black Pigment	3 g
	Titanium Dioxide	4 g
30	Yellow Iron Oxide Pigment	44 g
15	Red Iron Oxide Pigment	9 g
	Filler (Barium Sulphate)	170 g
35	Filler (Calcium Carbonate)	120 g
	Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g ⁻¹)	619 g
	Hydroxyalkylamide Curing Agent	23 g
40	20 Benzoin	4 g
	Polyethylene Wax	4 g

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of d(v,20) = 22 microns, d(v,50) = 42microns, d(v,70) = 52 microns, d(v,95) = 84 microns, d(v,99) = 106microns; and 62% < 50 microns.

5

- 35 -

Clear Polyester Gloss Base Composition

10

Carboxylic Acid-Functional Polyester Resin (AV = 35 mg KOH g⁻¹) 920 g

TGIC Curing Agent 60 g

Amide modified Polyester Oligomer Flow Aid 13 g

15

5 Phenolic Antioxidant 6 g

Benzoin 1 g

20

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of d(v,20) = 19 microns, d(v,50) = 40 microns, d(v,70) = 50 microns, d(v,95) = 80 microns, d(v,99) = 97 microns; and 68% < 50 microns.

25

Red Polyester/Epoxy Hybrid Gloss Base Composition

30

Titanium Dioxide 10 g

Bonarylamide Red Pigment 68 g

15 Filler (Barium Sulphate) 52 g

Filler (Calcium Carbonate) 52 g

35

Carboxylic Acid-Functional Polyester Resin (AV = 34 mg KOH g⁻¹) 605 g

Epoxy Resin Curing Agent (EEW = 610 g/mol) 247 g

Tetrabutylammonium Bromide Catalyst 2 g

40

20 Acrylic Flow Modifier 10 g

Benzoin 3 g

Polyethylene Wax 3 g

45

The ingredients were dry mixed in a blender and extruded at 110°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of d(v,20) = 20 microns, d(v,50) = 40 microns, d(v,70) = 52 microns, d(v,95) = 81 microns, d(v,99) = 98 microns; and 68% < 50 microns.

50

55

- 36 -

White Epoxy Gloss Base Composition

Titanium Dioxide	295 g
Epoxy-Functional Polymer (EEW = 530 g/mol)	657 g
Dicyandiamide Crosslinker	32 g
Amino Phenolic Catalyst	4 g
Acrylic Flow Modifier	10 g
Benzoin	2 g

The ingredients were dry mixed in a blender and extruded at 110°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of $d(v,20) = 20$ microns, $d(v,50) = 39$ microns, $d(v,70) = 52$ microns, $d(v,95) = 80$ microns, $d(v,99) = 96$ microns; and 66% < 50 microns.

Blue Polyester Colourant Additive Composition

The blue polyester gloss base composition described above was further milled and sieved to produce a powder with a particle size distribution of $d(v,50) = 5$ microns, $d(v,90) = 12$ microns, $d(v,99) = 13$ microns.

White Polyester Colourant Additive Composition

The white polyester gloss base composition described above was further milled and sieved to produce a powder with a particle size distribution of $d(v,50) = 5$ microns, $d(v,90) = 12$ microns, $d(v,99) = 13$ microns.

Agglomerated Blue Polyester Gloss Base Composition

Equal proportions of the blue and white polyester colourant additive compositions described above were blended together in a Henschel FM10 mixture for

5

- 37 -

10

30 minutes in total, with a water jacket taking the temperature to 54°C. The agglomerated powder was sieved to produce a powder having a particle size distribution of $d(v,20) = 10$ microns, $d(v,50) = 16$ microns, $d(v,70) = 25$ microns.

15

5 Polyester Matting Base Composition 1

Carboxylic Acid-Functional Polyester Resin (AV = 80 mg KOH g ⁻¹)	575 g
Hydroxyalkylamide Curing Agent	65 g
Phenolic Antioxidant	2 g
Benzoin	4 g
Acrylic Flow Modifier	16 g
Filler (Barium Sulphate)	325 g
Amide-modified Castor Oil Wax Rheological Agent	10 g
Polyethylene Wax	2 g

20

25

30

The ingredients were dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of $d(v,20) = 5$ microns, $d(v,50) = 11$ microns, $d(v,70) = 15$ microns, $d(v,95) = 28$ microns, $d(v,99) = 35$ microns; and 100% < 50 microns.

35

40

Polyester Matting Base Composition 2

20 The ingredients for polyester matting base composition 1 were dry dry mixed in a blender and extruded at 120°C. The extrudate was then impact milled and sieved to produce a powder with a particle size distribution of $d(v,20) = 10$ microns, $d(v,50) = 20$ microns, $d(v,70) = 27$ microns, $d(v,95) = 48$ microns, $d(v,99) = 62$ microns; and 96% < 50 microns.

45

50

25

55

Clear Polyester Gloss Mica Masterbatch Composition

Clear Polyester Gloss Base (see above)	750 g
Mica Pigment	250 g

The ingredients were fused together by use of a high speed Henschel mixer for 9 minutes at 1000 r.p.m. until a temperature of 70°C was reached inside the mixer. The mix was then left to cool to room temperature then discharged and sieved to produce a powder with a particle size distribution of $d(v,20) = 19$ microns, $d(v,50) = 40$ microns, $d(v,70) = 51$ microns, $d(v,95) = 79$ microns, $d(v,99) = 97$ microns; and 68% < 50 microns.

Dry Blend Additive 1

Aluminium Oxide	6 g
Aluminium Hydroxide	24 g

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

Dry Blend Additive 2

Aluminium Oxide	13.5 g
Aluminium Hydroxide	16.5 g

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

5

- 39 -

Dry Blend Additive 3

10

Aluminium Oxide 24 g

Aluminium Hydroxide 6 g

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

15

5

20

Dry Blend Additive 4

Aluminium Oxide 19.2 g

10 Aluminium Hydroxide 4.8 g

25

Wax-coated Silica 6.0 g

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

30

15

Dry Blend Additive 5

35

Aluminium Oxide 10 g

Wax-coated Silica 10 g

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

40

20

45

Dry Blend Additive 6

Aluminium Hydroxide 7 g

50

25 Wax-coated Silica 13 g

55

5

- 40 -

10

The ingredients were charged to a Moulinex II high-shear blender, mixed for 30 seconds, cooled and the mixing and cooling procedure repeated twice more to give a total of three operations.

15

5 Dry Blend Additive 7

Wax-coated Silica

20

Example (1)

Blue Polyester Matt Composition

25

10	Blue Polyester Gloss Base	865 g
	Polyester Matting Base 1	130 g
	Dry Blend Additive 1	5 g

30

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a matt finish was obtained. No variation in film appearance was observed over the range of conditions.

35

40

20

Example (2)

Yellow Polyester Matt Composition

45

	Yellow Polyester Gloss Base	867.8 g
	Polyester Matting Base 2	129.7 g
25	Dry Blend Additive 3	2.5 g

50

55

5

- 41 -

10

15

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a matt finish was obtained. No variation in film appearance was observed over the range of conditions.

20

Example (3)Blue Polyester Satin Composition

25

10	Blue Polyester Gloss Base	947.6 g
	Polyester Matting Base 1	47.4 g
	Dry Blend Additive 2	5 g

30

35

40

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes. A coating with a satin finish was obtained. No variation in film appearance was observed over the range of conditions.

20

Example (4)Grey Polyester Texture Composition

45

	Grey Polyester Gloss Base	975 g
	Ester-Modified Polyether Oligomer Texturing Additive (Troy Powdermate 508TEX)	20 g
25	Dry Blend Additive 2	5 g

50

55

- 42 -

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a textured finish was obtained. No variation in film appearance was observed over the range of conditions.

Example (5)**Grey Polyester Fine Texture Composition**

Grey Polyester Gloss Base	965 g
PTFE Texturing Additive (Hoechst Hostafon TF1702)	30 g
Dry Blend Additive 2	5 g

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a fine textured finish was obtained. No variation in film appearance was observed over the range of conditions.

Example (6)**Grey Polyester Coarse Texture Composition**

Grey Polyester Gloss Base	985 g
CAB Texturing Additive (Eastman Chemical CAB 551-0.2)	10 g
Dry Blend Additive 2	5 g

5

- 43 -

10

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a coarse textured finish was obtained. No variation in film appearance was observed over the range of conditions.

15

5

20

Example (7)10 Brown Polyester Coarse Texture Composition

25

Brown Polyester Gloss Base	991 g
Flow Aid (DSM Uralac P6188) micronised to d(v,50) = 40 microns	4 g
Dry Blend Additive 2	5 g

30

15

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a coarse textured finish was obtained. No variation in film appearance was observed over the range of conditions.

35

40

20

Example (8)

45

Grey Polyester Contrast Texture Composition

50

25

Grey Polyester Gloss Base	982 g
CAB Texturing Additive (Eastman Chemical CAB 551-0.2)	10 g
Titanium Dioxide	2 g

55

- 44 -

Red Iron Oxide Pigment	1 g
Dry Blend Additive 2	5 g

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a contrast textured finish (light grey with dark grey peaks appearing as an exaggerated sparkle) was obtained. No variation in film appearance was observed over the range of conditions.

Example (9)**Blue Polyester Matt Texture Composition**

Blue Polyester Gloss Base	845 g
Polyester Matting Base 1	130 g
Ester-Modified Polyether Oligomer Texturing Additive (Troy Powdermate 508TEX)	20 g
Dry Blend Additive 2	5 g

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a matt textured finish was obtained. No variation in film appearance was observed over the range of conditions.

5

- 45 -

Example (10)

10

Blue Polyester Metallic Composition

Blue Polyester Gloss Base	965 g
Mica Pigment	30 g
5 Dry Blend Additive 4	5 g

15

20 The ingredients were dry blended by use of a Waring Laboratory high shear
blender and mixed for two 5 second periods. When the powder mixture was sprayed
at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium
10 panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a
25 coating with a metallic finish was obtained. No variation in film appearance was
observed over the range of conditions.

30

Example (11)15 Blue Polyester Metallic Sparkle Composition

Blue Polyester Gloss Base	900 g
35 Clear Polyester Gloss Mica Masterbatch	100 g
Dry Blend Additive 2	5 g

40

20 The ingredients were dry blended by use of a Waring Laboratory high shear
blender and mixed for two 5 second periods. When the powder mixture was sprayed
at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium
45 panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a
coating with a metallic sparkle finish was obtained. No variation in film appearance
25 was observed over the range of conditions.

50

55

5

- 46 -

Example (12)Blue Polyester Matt Metallic Composition

10

Blue Polyester Gloss Base 840 g

Polyester Matting Base 1 125 g

15

5 Mica Pigment 30 g

Dry Blend Additive 2 5 g

20

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a matt metallic finish was obtained. No variation in film appearance was observed over the range of conditions.

25

30

15 Example (13)Brown Polyester Antique Composition

35

Brown Polyester Gloss Base 945 g

Ester-Modified Polyether Oligomer Texturing additive 20 g
(Troy Powdermate 508TEX)

40

20 Mica Pigment 30 g

Dry Blend Additive 2 5 g

45

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a

25

50

55

- 47 -

coating with an antique finish was obtained. No variation in film appearance was observed over the range of conditions.

Example (14)5 Polyester Mixed Colour Composition

Blue Polyester Gloss Base	497.5 g
White Polyester Gloss Base	497.5 g
Dry Blend Additive 2	5 g

10 The ingredients were dry blended by use of a Waring Laboratory high shear
25 blender and mixed for two 5 second periods. When the powder mixture was sprayed
at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium
panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a
30 coating with a mixed (speckled) colour finish was obtained. No variation in film
15 appearance was observed over the range of conditions.

35 Example (15)White Epoxy Texture Composition

White Epoxy Gloss Base	975 g
20 Ester-Modified Polyether Oligomer Texturing Additive (Troy Powdermate 508TEX)	20 g
Dry Blend Additive 2	5 g

45 The ingredients were dry blended by use of a Waring Laboratory high shear
25 blender and mixed for two 5 second periods. When the powder mixture was sprayed
50 at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto aluminium

- 48 -

panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a textured finish was obtained. No variation in film appearance was observed over the range of conditions.

5 Example (16)

Red Hybrid Metallic Composition

Red Hybrid Gloss Base	965 g
Mica Pigment	30 g
Dry Blend Additive 2	5 g

10

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a metallic finish was obtained. No variation in film appearance was observed over the range of conditions.

Example 17

Blue Polyester Matt Composition

Blue Polyester Gloss Base	867 g
Polyester Matting Base 1	130 g
Dry Blend Additive 5	3 g

The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium

5

- 49 -

10

panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a matt finish was obtained. No variation in film appearance was observed over the range of conditions.

15

5 Example 18

Blue Polyester Satin Composition

20

Blue Polyester Gloss Base	948 g
Polyester Matting Base 1	47 g
Dry Blend Additive 6	5 g

25

- 10 The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a coating with a satin finish was obtained. No variation in film appearance was observed over the range of conditions.

30

35

Example 19

Yellow Polyester Matt Composition

40

Yellow Polyester Gloss Base	867 g
20 Polyester Matting Base 1	130 g
Dry Blend Additive 7	3 g

45

- The ingredients were dry blended by use of a Waring Laboratory high shear blender and mixed for two 5 second periods. When the powder mixture was sprayed at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a

50

55

5

- 50 -

10

coating with a matt finish was obtained. No variation in film appearance was observed over the range of conditions.

Example 20

15

5 Pale Blue Tinted Gloss Composition

White Polyester Gloss Base 967 g

Blue Polyester Colourant Additive 30 g

20

Dry Blend Additive 2 3 g

25

The ingredients were dry blended by use of a Waring Laboratory high shear
10 blender and mixed for two 5 second periods. When the powder mixture was sprayed
at an application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium
panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a
coating with a single homogeneous pale blue colour was obtained. No variation in film
30 appearance was observed over the range of conditions.

15

Example 21

35

Blue Polyester Metallic Composition

Agglomerated Blue Polyester Gloss base 967 g

Mica pigment 30 g

40

20 Dry Blend Additive 2 3 g

45

The ingredients were dry blended by use of a Waring Laboratory high shear blender
and mixed for two 5 second periods. When the powder mixture was sprayed at an
application voltage of -50 to -100kV (Ransberg Gema PG 1 gun) onto Aluminium
panels to a film thickness of 50-110 microns and stoved at 200°C for 15 minutes, a
25 coating with a blue metallic colour was obtained. No variation in film appearance was
observed over the range of conditions.

50

55

Claims

5

10

15

20

25

30

35

40

45

50

55

5

- 51 -

10

CLAIMS

1. A powder coating composition which comprises one or more film-forming polymeric components

15

- 5 (p1) having a d(v,50) in the range of from 25 to 50 microns, or
(p2) having a d(v,70) in the range of from 25 to 70 microns, or
(p3) in which no more than 70% by volume of the particles are less than 50
20 microns,

such component(s) constituting the major proportion of the composition, and which

- 10 composition incorporates by dry blending at least one appearance-modifying
additive component and a further additive component comprising wax-coated silica or
25 consisting of alumina together with aluminium hydroxide.

2. A powder coating composition which comprises a film-forming polymeric component and which incorporates, by dry blending,

30

- 15 • a gloss-reducing component,
a texturing component,
35 a metallic or mica component,
a colouring pigment or pigment concentrate component, or
a further film-forming polymeric material compatible with the first film-forming
40 20 polymeric material and differing in colouration therefrom,
or two or more such components, and
• a further additive selected from
45 alumina together with aluminium hydroxide,
wax-coated silica together with alumina and/or with aluminium hydroxide,
25 wax-coated silica,

50

55

5

- 52 -

and wherein at least the major proportion of the composition comprises film-forming
polymeric material

10

(p1) having a d(v,50) in the range of from 25 to 50 microns, or

(p2) having a d(v,70) in the range of from 25 to 70 microns and a d(v,20) in
the range of from 8 to 30 microns, or

15

5

(p3) in which no more than 70% by volume of the particles are less than 50
microns.

20

3. A powder coating composition which comprises a dry-blended mixture of
the following particulate components:

10 (a) a coloured film-forming polymeric material having a d(v,50) in the range of from
25 to 50 microns and a d(v,99) in the range of from 60 to 120 microns, or in
which no more than 70% by volume of the particles are less than 50 microns,

25

(b) at least one appearance-modifying component selected from

30

(1) a gloss-reducing additive component

15

(2) a texturing agent component

(3) a metallic or mica pigment optionally bonded to a film-forming polymeric
material

35

(4) a colouring pigment component, or

(5) a film-forming polymeric material compatible with the film-forming

40

20

component (a) and different in colour therefrom, in which at least 90%
by volume of the particles are no more than 20 microns, and

(6) a film-forming polymeric material compatible with the film-forming

45

component (a) and different in colour therefrom, and having a d(v,50) in
the range of from 25 to 50 microns and a d(v,99) in the range of from 60

25

to 120 microns, or in which no more than 70% by volume of the particles
are less than 50 microns,

50

55

5

- 53 -

(c) a further additive selected from

10

(i) alumina together with aluminium hydroxide

(ii) alumina together with wax-coated silica

(iii) aluminium hydroxide together with wax-coated silica.

15

5 (iv) alumina together with aluminium hydroxide and wax-coated silica

(v) wax-coated silica,

wherein the composition contains at least 60% by weight of film-forming polymeric

20

material having a $d(v,50)$ in the range of from 25 to 50 microns and a $d(v,99)$ in the

range of from 60 to 120 microns or in which no more than 70% by volume of the

10 particles are less than 50 microns .

25

4. A powder coating composition as claimed in any one of claims 1 to 3,

which includes a metallic or mica component comprising a metallic or mica pigment

bonded to an uncoloured film-forming polymeric material having a $d(v,50)$ in the range

30

of from 15 to 50 microns or a $d(v,70)$ in the range of from 20 to 70 microns.

15 5. A powder coating composition as claimed in any one of claims 1 to 4,

which includes a metallic or mica pigment component containing 2 to 40% by weight of

35

metallic or mica pigment bonded to film-forming polymeric material.

6. A powder coating composition as claimed in any one of claims 1 to 5,

wherein the composition comprises at least 70% by weight of coloured film-forming

40

20 polymeric material of the particle size (p1), (p2) or (p3).

7. A powder coating composition as claimed in any one of claims 1 to 6,

which contains up to 30% by weight of gloss-reducing additive based on the total

45

weight of the composition.

8. A powder coating composition as claimed in claim 7, wherein the

25 content of gloss-reducing additive is up to 20% by weight based on the total weight of

50

the composition.

55

5

- 54 -

10

15

9. A powder coating composition as claimed in any one of claims 1 to 8, wherein the film-forming polymeric material of the specified particle size (p1), (p2) or (p3) comprises acid-functional polyester, and the gloss-reducing component comprises an uncoloured film-forming polymeric material of reduced particle size and comprising an acid-functional polyester of higher functionality.

20

10. A powder coating composition as claimed in claim 9, wherein the gloss-reducing additive has a particle size such that at least 90% by volume of particles are less than 50 microns and the mean particle size is less than 30 microns.

25

11. A powder coating composition as claimed in any one of claims 1 to 10, which contains up to 5% by weight of texturing agent based on the total weight of the composition.

30

12. A powder coating composition as claimed in any one of claims 1 to 11, which contains up to 10% by weight of metallic or mica pigment based on the total weight of the composition.

35

13. A powder coating composition as claimed in any one of claims 1 to 12, which contains up to 5% by weight, based on the total weight of the composition, of colouring pigment or of coloured film-forming polymeric material that is compatible with the main film-forming component and in which at least 90% by volume of the particles are no more than 20 microns.

40

14. A powder coating composition as claimed in any one of claims 1 to 13, wherein the amount of further additive component (c) is up to 5% by weight based on the weight of the total composition.

45

15. A powder coating composition as claimed in claim 14, wherein the amount of further additive component (c) is up to 2% by weight based on the weight of the total composition.

50

55

5

- 55 -

10

15

20

25

30

35

40

45

50

55

16. A powder coating composition as claimed in any one of claims 1 to 15, wherein the further additive component (c) is selected from

- (i) alumina together with aluminium hydroxide,
- (ii) alumina together with wax-coated silica,
- (iii) alumina together with aluminium hydroxide and wax-coated silica.

17. A powder coating composition as claimed in any one of claims 1 to 16, wherein the film-forming polymeric material of the specified particle size (p1), (p2) or (p3) is or includes a powder in the form of a fused or bonded agglomerate consisting of composite particles.

18. A powder coating composition as claimed in any one of claims 1 to 17, wherein the major proportion of the composition comprises film-forming polymeric material having a d(v,50) in the range of from 35 to 45 microns and a d(v,99) in the range of from 80 to 100 microns.

19. A powder coating composition as claimed in any one of claims 1 to 18, wherein the major proportion of the composition comprises film-forming polymeric material having a d(v,70) in the range of from 25 to 70 microns and wherein the further additive (c) consists of or includes wax-coated silica.

20. A powder coating composition as claimed in any one of claims 1 to 19, wherein the major proportion of the composition comprises film-forming polymeric material having a d(v,70) in the range of from 25 to 70 microns and wherein the composition includes a gloss-reducing component, a texturing component, a metallic or mica component bonded to a film-forming polymeric material, a non-bonded metallic or mica pigment (in which case the specified film-forming polymeric material is or includes a fused or bonded agglomerate consisting of composite particles), a colouring pigment or pigment concentrate, or a film-forming polymeric material compatible with the film-forming component constituting the major proportion of the composition and different in

5

- 56 -

10

colour therefrom and in which at least 90% by volume of the particles are no more than 20 microns, or two or more such appearance-modifying components, and alumina together with aluminium hydroxide.

15

21. A powder coating composition as claimed in any one of claims 1 to 20, wherein the major proportion of the composition comprises film-forming polymeric material having a $d(v,70)$ in the range of from 25 to 70 microns and is or includes a powder in the form of a fused or bonded agglomerate formed from smaller-sized film-forming particles.

20

25

22. A powder coating composition as claimed in any one of claims 1 to 21, wherein the major proportion of the composition comprises film-forming polymeric material having a $d(v,70)$ in the range of from 40 to 60 microns and a $d(v,20)$ in the range of from 15 to 25 microns.

30

23. A powder coating composition as claimed in any one of claims 1 to 22, which includes
- 15 a gloss-reducing component and a texturing component,
a gloss-reducing component and a metallic or mica component,
35 a texturing component and a metallic or mica component, or
a texturing component and a colouring pigment.

35

40

24. A kit comprising the following separate particulate components for dry blend mixing into powder coating compositions for the preparation of powder coatings in a number of different finishes:

45

- at least one appearance-modifying additive component selected from
 - (1) a gloss-reducing component,
 - (2) a texturing component,
 - 25 (3) a metallic or mica pigment component, and
 - 50 (4) a colouring pigment or pigment concentrate component, and

50

55

5

- 57 -

(5) a coloured film-forming polymeric component having a $d(v,90)$ of no more than 20 microns, and

10

- a further additive selected from

(i) alumina together with aluminium hydroxide

5

(ii) alumina together with wax-coated silica

15

(iii) aluminium hydroxide together with wax-coated silica,

(iv) alumina together with aluminium hydroxide and wax-coated silica

20

(v) wax-coated silica,

or two or more such additives.

10

25. A kit as claimed in claim 24, which includes

25

- components (1), (2) and (3)

and optionally

- one or more colouring pigments and/or pigment concentrates (4) and/or coloured film-forming polymeric materials (5).

30

15

26. A kit as claimed in claim 24 or claim 25, wherein an appearance-modifying additive is in the form of a bonded masterbatch in which a non-film-forming additive is bonded to film-forming polymeric material.

35

27. A kit as claimed in any one of claims 24 to 26, which includes an uncoloured film-forming polymeric component.

40

20

28. A process for modifying a standard gloss powder coating composition to give a desired finish, which comprises dry blending into the composition

(1) a gloss-reducing component,

45

(2) a texturing component,

(3) a metallic or mica pigment component,

25

(4) a colouring pigment or pigment concentrate component, or

50

55

5

- 58 -

10

- (5) a film-forming polymeric material compatible with the film-forming polymeric material of the standard gloss powder coating composition and differing in colouration therefrom,

or two or more such components,

15

- 5 and a further component comprising wax-coated silica or consisting of alumina together with aluminium hydroxide.

20

29. A process for preparing a powder coating composition in a desired finish, which comprises dry blending the following particulate components

- (a) a coloured film-forming polymeric material, and

10

- (b) (1) a gloss-reducing component,

25

- (2) a texturing component,

- (3) a metallic or mica component,

- (4) a colouring pigment or pigment concentrate component, or

30

- (5) a further film-forming polymeric material compatible with the first film-

15

forming polymeric material and differing in colouration therefrom,

or two or more such components, and

35

- (c) a further additive selected from

alumina together with aluminium hydroxide,

wax-coated silica together with alumina and/or with aluminium hydroxide,

40

20

wax-coated silica,

and wherein at least the major proportion of the composition comprises film-forming polymeric material

45

- (p1) having a d(v,50) in the range of from 25 to 50 microns, or

- (p2) having a d(v,70) in the range of from 25 to 70 microns and a d(v,20) in

25

the range of from 8 to 30 microns, or

50

55

5

- 59 -

(p3) in which no more than 70% by volume of the particles are less than 50 microns.

10

30. A powder coating composition when prepared by a process as claimed in claim 28 or claim 29.

15

5 31. A process for powder coating a substrate, characterised in that a composition according to any one of claims 1 to 23 or claim 30 is applied to the substrate and heated to form a continuous coating.

20

32. A substrate coated by a process as claimed in claim 31.

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/GB 99/02105

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D5/03 C09D167/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5 491 202 A (UMEHARA TAKAFUMI ET AL) 13 February 1996 (1996-02-13) column 2, line 51 - column 6, line 60 column 6, line 61 - column 7, line 5 column 7, line 15 - line 42	1-3, 19, 22, 23
A	US 5 015 671 A (ONO KAZUYA ET AL) 14 May 1991 (1991-05-14) column 1, line 54 - column 2, line 68; claims 1-7	1-3
A	EP 0 003 932 A (RHONE-POULENC IND) 5 September 1979 (1979-09-05) page 1, line 5 - line 10 page 2, line 26 - line 35 page 4, line 1 - page 5, line 19 page 8, line 17 - page 9, line 20 -/-	1-3, 17

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

Special categories of cited documents

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "Z" document member of the same patent family

Date of the actual completion of the international search

23 September 1999

Date of mailing of the international search report

30/09/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel: (+31-70) 340-2040, Tx: 31 651 epo m,
Fax: (+31-70) 340-3016

Authorized officer

Miller, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/02105

C. (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 372 860 A (COURTAULDS COATINGS LTD) 13 June 1990 (1990-06-13) cited in the application ----	1
A	WO 94 11446 A (COURTAULDS COATINGS HOLDINGS ; KITTLE KEVIN JEFFREY (GB); RUSHMAN P) 26 May 1994 (1994-05-26) cited in the application ----	1
A	GB 1 545 780 A (VEBA CHEMIE AG) 16 May 1979 (1979-05-16) cited in the application -----	1

1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/02105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5491202 A	13-02-1996	JP 6293867 A	21-10-1994
US 5015671 A	14-05-1991	JP 1995780 C	08-12-1995
		JP 3160064 A	10-07-1991
		JP 7013206 B	15-02-1995
		CA 2007056 A	17-05-1991
EP 0003932 A	05-09-1979	FR 2417533 A	14-09-1979
		BR 7901031 A	02-10-1979
		DK 70779 A	21-08-1979
		ES 477842 A	15-12-1979
		IE 47924 B	25-07-1984
		JP 1247833 C	16-01-1985
		JP 54158441 A	14-12-1979
		JP 59023580 B	02-06-1984
		US 4371638 A	01-02-1983
		US 4414279 A	08-11-1983
EP 0372860 A	13-06-1990	AU 643191 B	11-11-1993
		AU 4648389 A	26-06-1990
		CA 2004213 A	02-06-1990
		DE 68922898 D	06-07-1995
		DE 68922898 T	21-12-1995
		DK 104491 A	31-05-1991
		ES 2074083 T	01-09-1995
		WO 9006345 A	14-06-1990
		GB 2226824 A,B	11-07-1990
		GR 3017117 T	30-11-1995
		JP 4504431 T	06-08-1992
		KR 152066 B	01-10-1998
		PT 92481 A,B	29-06-1990
		TR 26410 A	11-02-1995
		US 5856378 A	05-01-1999
		US 5319001 A	07-06-1994
WO 9411446 A	26-05-1994	AU 682159 B	25-09-1997
		AU 5427294 A	08-06-1994
		CA 2148842 A	26-05-1994
		CN 1088599 A	29-06-1994
		CZ 9501171 A	13-12-1995
		EP 0667889 A	23-08-1995
		FI 952178 A	05-05-1995
		GB 2287468 A,B	20-09-1995
		HK 1006031 A	05-02-1999
		HU 72031 A	28-03-1996
		JP 8503239 T	09-04-1996
		NO 951764 A	20-06-1995
		NZ 257600 A	24-02-1997
		PL 308549 A	21-08-1995
		SG 45216 A	16-01-1998
		SK 56695 A	11-10-1995
		TR 27298 A	29-12-1994
		US 5635548 A	03-06-1997
		ZA 9308233 A	29-06-1994
GB 1545780 A	16-05-1979	DE 2507786 A	02-09-1976
		AU 500595 B	24-05-1979
		AU 1136176 A	01-09-1977

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern 1st Application No
PCT/G8 99/02105

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1545780 A		BE 838788 A	16-06-1976
		CH 602196 A	31-07-1978
		ES 445330 A	16-06-1977
		FR 2301581 A	17-09-1976
		IT 1055388 B	21-12-1981
		JP 51107336 A	22-09-1976
		NL 7601739 A	24-08-1976
		SE 7602071 A	23-08-1976
		ZA 7601028 A	23-02-1977